

**PCT**WORLD INTELLECTUAL PRO  
International

WO 9608553A1

## INTERNATIONAL APPLICATION PUBLISHED UNDE

(51) International Patent Classification 6 : <b>C11D 3/37, 3/16</b>	<b>A1</b>	(11) International Publication Number: <b>WO 96/08553</b>
		(43) International Publication Date: <b>21 March 1996 (21.03.96)</b>

(21) International Application Number: <b>PCT/US95/05813</b>	(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).
(22) International Filing Date: <b>8 May 1995 (08.05.95)</b>	
(30) Priority Data: 08/304,571 12 September 1994 (12.09.94) US 08/390,532 16 February 1995 (16.02.95) US	
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**(54) Title: RINSE AID FOR PLASTICWARE****(57) Abstract**

A rinse aid composition for use on plasticware is herein described which requires lower concentration of conventional hydrocarbon surfactants, exhibits adequate sheeting on the plasticware and acceptable drying time which prior rinse aids have failed to provide without special handling. The compositions described contain hydrocarbon surfactants and a polyether or polybetaine polysiloxane copolymer surfactant alone or in combination with a fluorinated hydrocarbon surfactant. The composition may be formulated as a solid or liquid suitable for dilution to form an aqueous rinse used to contact the plasticware in a warewashing machine.

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RINSE AID FOR PLASTICWARECROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of  
5 application Serial No. 08/304,571 filed September 12,  
1994.

Field of the Invention

The invention relates to warewashing processes  
and chemicals used in washing plastic cookware, dishware  
10 and flatware. More particularly, the invention relates  
to primarily organic materials that can be added to  
water to promote a sheeting action in an aqueous rinse  
used after an alkaline detergent cycle. Such aqueous  
rinse aids promote effective sheeting to result in  
15 removal of aqueous rinse materials and solids contained  
therein from plastic cookware, dishware and flatware in  
acceptable drying time without cracking the plasticware.

Background of the Invention

20 Mechanical warewashing machines have been  
common in the institutional and household environments  
for many years. Such automatic warewashing machines  
clean dishes using two or more cycles which can include  
initially a wash cycle followed by a rinse cycle. Such  
25 dishwashers can also utilize soak cycle, prewash cycle,  
scrape cycle, second wash cycle, a rinse cycle, a  
sanitizing cycle and a drying cycle, if required. Such  
cycles can be repeated if needed and additional cycles  
can be used. After passing through a wash, rinse and  
30 dry cycle, dishware, cups, glasses, etc., can exhibit  
spotting that arises from the uneven draining of the  
water from the surface of the ware after the rinse step.  
Spotting is aesthetically unacceptable in most consumer  
and institutional environments.

35 In order to substantially prevent the  
formation of spotting rinse agents have commonly been  
added to water to form an aqueous rinse which is sprayed  
on the dishware after cleaning is complete. The precise  
mechanism through which rinse agents work is not

established. One theory holds that the surfactant in the rinse aid is absorbed on the surface at temperatures at or above its cloud point, and thereby reduces the solid-liquid interfacial energy and contact angle. This 5 leads to the formation of a continuous sheet which drains evenly from the surface and minimizes the formation of spots. Generally, high foaming surfactants have cloud points above the temperature of the rinse water, and, according to this theory, would not promote 10 sheet formation, thereby resulting in spots. Moreover, high foaming materials are known to interfere with the operation of the warewashing machine. Common rinse aid formulas are used in an amount of less than about 1,000 parts preferably less than 500 parts, commonly 50 to 200 15 parts per million of active materials in the aqueous rinse. Rinse agents available in the consumer and institutional markets comprise liquid or solid forms which are typically added to, dispersed or dissolved in water to form an aqueous rinse. Such dissolution can 20 occur from a rinse agent installed onto the dish rack. The rinse agent can be diluted and dispensed from a dispenser mounted on or in the machine or from a separate dispenser that is mounted separately but cooperatively with the dish machine.

25 Commonly available commercial rinse agents typically comprise a low foaming surface active agent made from homopolymers or copolymers of an alkylene oxide such as ethylene oxide or propylene oxide or mixtures thereof. Typically, the surfactants are formed 30 by reacting an alcohol, a glycol, a carboxylic acid, an amine or a substituted phenol with various proportions and combinations of ethylene oxide and propylene oxide to form both random and block copolymer substituents.

35 The commonly available rinse agents have primarily focused on reducing spotting and filming on surfaces such as glass, ceramics, china and metal. However, plastic dishware is more commonly used now,

especially in the institutional market. A special problem for rinse aid surfactants used for plasticware is the attack and crazing of the ware. Block copolymer surfactants do not seem to attack plastics as strongly 5 as fatty alcohol or alkyl phenol-based nonionic surfactants. Linear alkoxylates show they do not attack plexiglass, polystyrene, or Tupperware<sup>®</sup>, common utensil plastics. Nevertheless, current surfactants have not provided the desired sheeting in an acceptable drying 10 time following the rinse cycle.

U.S. Patent 5,298,289 describes the treatment and after-treatment of surfaces, especially metals, with derivatives of polyphenol compounds. These compositions are also said to be useful in treating plastic and 15 painted surfaces to improve rinsability without water breaks. The surfactants employed are a combination of previously known anionic and nonionic surfactants.

Liquid dishwashing detergent compositions are described in U.S. Patent 4,452,646 containing highly 20 ethoxylated nonionic surfactants to reduce spotting and filming on surfaces such as glass, ceramics and metal.

European Patent Publication 0,432,836 describes the use of alkyl polyglycoside surfactants in rinse aid compositions on polycarbonate.

25 Fluorinated surfactants are described in U.S. Patent 4,089,804 where a non-ethoxylated fluoroaliphatic sulfonamide alcohol is added to typical fluorinated hydrocarbon surfactants as a synergist. The compositions are described as useful in a wide variety 30 of industries, e.g., household cosmetic and personal products. Rinse aid for dishwashing is mentioned.

Certain organosilanes have been described in 35 rinse aid compositions where the organosilane contains either a nitrogen, phosphorous or sulfur cationic group in combination with an anion, e.g. a monofunctional organic acid. U.S. Patent 4,005,024 describes such

compounds in a rinse aid composition to attract specific soil particles.

Aminosilanes have been described with a low foaming ethoxylated nonionic surfactant in rinse aid compositions in automatic dishwashing machines.

None of the fluorinated surfactants or silanes described in rinse aid compositions have focused on their use in plasticware.

Surprisingly, we have found that by adding a polyether or polybetaine polysiloxane nonionic or amphoteric surfactant alone or in combination with a fluorinated hydrocarbon surfactant, especially an ethoxylated fluorinated aliphatic sulfonamide alcohol, to a conventional rinse aid composition containing hydrocarbon surfactants, the resulting rinse agent provides excellent sheeting properties on plasticware without attacking or crazing the plastic and, more importantly, providing dried, non-spotted plasticware in acceptable time following the rinse cycle.

20

#### Summary of the Invention

Accordingly, the present invention is a rinse aid composition for plasticware, formulated as a dilutable liquid, gel or solid concentrate and, when diluted, forming an aqueous rinse, and including in addition to conventional rinse aid surfactants, e.g. hydrocarbon surfactants, about 0.1 to 10 wt-% of a polyalkylene oxide-modified polydimethylsiloxane or a polybetaine-modified polysiloxane, optionally in combination with about 0.1 to 10 wt-% of a fluorinated hydrocarbon nonionic surfactant.

A second aspect of the present invention is a method of cleaning plasticware by: (a) first contacting the ware with an alkaline aqueous cleaning agent in a warewashing machine at 100-180°F to produce cleaned plasticware, and (b) contacting the cleaned plasticware with an aqueous rinse containing a major proportion of

an aqueous diluent having about 2 to 100 parts per million of hydrocarbon surfactants, and about 0.01 to 10 parts per million of a polyalkylene oxide-modified polydimethylsiloxane or polybetaine-modified polysiloxane, optionally in combination with about 0.01 to 10 parts per million of a fluorinated hydrocarbon surfactant, e.g. an ethoxylated fluoroaliphatic sulfonamide alcohol.

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#### Detailed Description of the Invention

For the purpose of this invention, the term "rinse agent" includes concentrate materials that are diluted with an aqueous stream to produce an aqueous rinse. Accordingly, an aqueous rinse agent is an aqueous material that is contacted with ware in a rinse cycle. A sheeting agent is the polymeric material used to promote the even draining of the aqueous rinse. Sheetng is defined as forming a continuous, evenly draining film, leaving virtually no spots or film upon the evaporation of water. For the purpose of this invention, the term "dish" or the term "ware" is used in the broadest sense of the term to refer to various types of articles used in the preparation, serving, consumption, and disposal of food stuffs including pots, pans, trays, pitchers, bowls, plates, saucers, cups, glasses, forks, knives, spoons, spatulas, and other glass, metal, ceramic, plastic composite articles commonly available in the institutional or household kitchen or dining room.

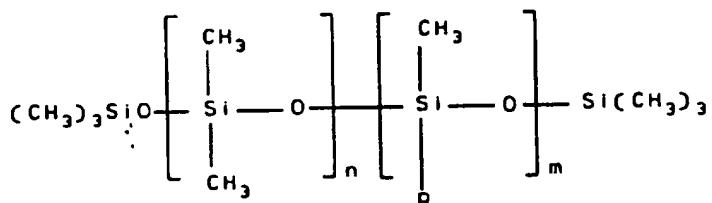
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Since the present invention focuses on plastic articles, the term "plasticware" includes the above articles made from, e.g., polycarbonate, melamine, polypropylene, polyester resin, polysulfone, and the like.

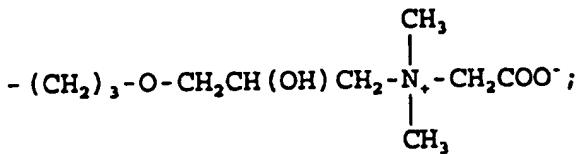
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The siloxane surfactant employed as an additive in the present invention alone or in combination with a fluorochemical surfactant described

polybetaine-modified polysiloxane amphoteric surfactant. Both, preferably, are linear polysiloxane copolymers to which polyethers or polybetaines have been grafted through a hydrosilation reaction. This process results 5 in an alkyl-pendant (AP type) copolymer, in which the polyalkylene oxide groups, for example, are attached along the siloxane backbone through a series of hydrolytically stable Si-C bonds. These products have the general formula:



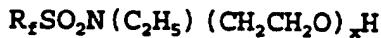
wherein R is  $-(\text{CH}_2)_3-\text{O}-(\text{EO})_x-(\text{PO})_y-\text{Z}$  or



15 EO is ethyleneoxy, PO is 1,2-propyleneoxy, Z is hydrogen or alkyl of 1-6 carbon atoms, and the weight ratio in % of EO:PO may vary from 100:0 to 0:100. A broad range of 20 surfactants have been developed varying x and y above and coefficients n and m. Preferably, n is 0 or 1 and m is at least 1. More preferred are the siloxanes where Z is hydrogen, methyl or butyl and the weight ratio of 25 EO:PO is 100:0 to 40:60. Particularly valuable are the siloxane surfactants herein described and known as SILWET<sup>®</sup> surfactants available from Union Carbide or ABIL<sup>®</sup> polyether or polybetaine polysiloxane copolymers available from Goldschmidt Chemical Corp. The 30 particular siloxanes used in the present invention are described as having, e.g., low surface tension, high wetting ability and excellent lubricity. For example,

wetting ability and excellent lubricity. For example, these surfactants are said to be among the few capable of wetting polytetrafluoroethylene surfaces.

The fluorochemical surfactant employed as an 5 additive in the present invention in combination with a silane, defined above, is a nonionic fluorohydrocarbon, such as, for example, fluorinated alkyl polyoxyethylene ethanols, fluorinated alkyl alkoxylate and fluorinated alkyl esters. These Fluorad™ surfactants are available 10 from 3M. As a fluorinated alkyl polyoxyethylene ethanol, included as a preferred surfactant is a polyoxyethylene adduct of a fluoroaliphatic sulfonamide alcohol which has excellent wetting, spreading and levelling properties. These surfactants may be 15 described as having the formula:



wherein  $R_f$  is  $C_nF_{2n+1}$  in which n is 6-10 and x may vary from 10 to 20. Particularly valuable is the surfactant where n is 8 and x is 14. This particular surfactant 20 identified as FC-170C is also available from 3M.

Although fluorocarbon surfactants and silicone surfactants have been known to be good wetting agents and used individually in rinse aid formulations, there is no description of their being used effectively in 25 plasticware as rinse aids. We have found in the present invention that the use of certain polysiloxane copolymers in a mixture with hydrocarbon surfactants provide excellent rinse aids on plasticware. We have also found that the combination of certain silicone 30 polysiloxane copolymers and fluorocarbon surfactants with conventional hydrocarbon surfactants also provide excellent rinse aids on plasticware. This combination has been found to be better than the individual components except with certain polyalkylene oxide- 35 modified polydimethylsiloxanes and polybetaine polysiloxane copolymers of the present invention where the effectiveness is about equivalent. Therefore, the

preferred embodiments of the present invention encompass the polysiloxane copolymers alone and the combination with the fluorocarbon surfactant preferably involves polyether polysiloxanes, the nonionic siloxane 5 surfactants. The amphoteric siloxane surfactants, the polybetaaine polysiloxane copolymers may be employed alone as the additive in the conventional rinse aids to provide the same results.

Since the use of the above siloxane additives 10 alone or in combination with the fluorocarbon are applicable to all conventional rinse aid formulations, the following description of ingredients and rinse aid formulations is illustrative only and not limiting of the present invention.

15 An example of hydrocarbon surfactants in conventional rinse aid formulations are nonionic surfactants, typically a polyether compound prepared from ethylene oxide, propylene oxide, in a homopolymer or a block or heteric copolymer. Such polyether 20 compounds are known as polyalkylene oxide polymers, polyoxyalkylene polymers, or polyalkylene glycol polymers. Such sheeting or rinse agents have a molecular weight in the range of about 500 to about 15,000. Certain types of polyoxypropylene- 25 polyoxyethylene glycol polymer rinse aids have been found to be particularly useful. Those surfactants comprising at least one block of a polyoxypropylene and having at least one other block of polyoxyethylene attached to the polyoxypropylene block. Additional 30 blocks of polyoxyethylene or polyoxypropylene can be present in a molecule. These materials having an average molecular weight in the range of about 500 to about 15,000 are commonly available as PLURONIC® manufactured by the BASF Corporation and available under 35 a variety of other trademarks of their chemical suppliers. In addition, rinse aid compositions called PLURONIC® R (reverse pluronic structure) are also useful

in the rinse aids of the invention. Additionally, rinse aids made by reacting ethylene oxide or propylene oxide with an alcohol anion and an alkyl phenol anion, a fatty acid anion or other such anionic material can be useful.

5 One particularly useful rinse aid composition can comprise a capped polyalkoxylated C<sub>6-24</sub> linear alcohol. The rinse aids can be made with polyoxyethylene or polyoxypropylene units and can be capped with common agents forming an ether end group. One particularly

10 useful species of this rinse aid is a benzyl ether of a polyethoxylated C<sub>12-14</sub> linear alcohol; see U.S. Patent No. 3,444,247. Alcohol ethoxylates having EO and PO blocks can be particularly useful since the stereochemistry of these compounds can permit occlusion by urea, a feature

15 useful in preparing solid rinse aids.

Particularly useful polyoxypropylene polyoxyethylene block polymers are those comprising a center block of polyoxypropylene units and blocks of polyoxyethylene units to each side of the center block.

20 These copolymers have the formula shown below:



wherein m is an integer of 21 to 54; n is an integer of 7 to 128. Additional useful block copolymers are block polymers having a center block of polyoxyethylene units

25 and blocks of polyoxypropylene units to each side of the center block. The copolymers have the formula as shown below:



wherein m is an integer of 14 to 164 and n is an integer

30 of 9 to 22.

In the preparation of conventional rinse aid compositions, a hydroscopic agent is often employed in the formulation. Such an agent may also be used in the present invention.

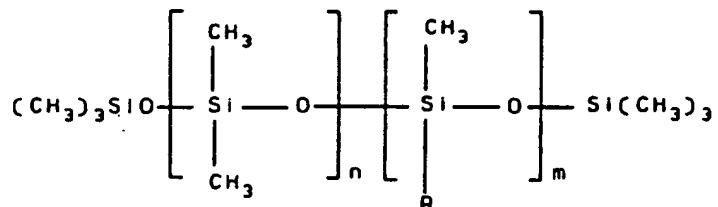
35 Hydroscopy is a property that relates to the ability of materials to improve the solubility or miscibility of a substance in liquid phases in which the

substance tends to be insoluble. Substances that provide hydrotropy are called hydrotropes and are used in relatively lower concentrations than the materials to be solubilized.

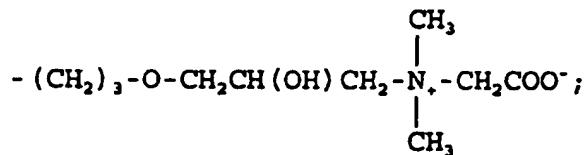
5       A hydrotrope modifies the solvent to increase the solubility of an insoluble substance or creates micellar or mixed micellar structures resulting in a stable suspension of the insoluble substance in the solvent. The hydrotropic mechanism is not thoroughly  
10      understood. Apparently either hydrogen bonding between primary solvent, in this case water, and the insoluble substance are improved by the hydrotrope or the hydrotrope creates a micellar structure around the insoluble composition to maintain the material in a  
15      suspension/solution. In this invention, the hydrotropes are most useful in maintaining a uniform solution of the cast rinse composition both during manufacture and when dispersed at the use location. The combination of the polyalkylene oxide materials and the casting aids tends  
20      to be partially incompatible with aqueous solution and can undergo a phase change or phase separation during storage of the solution. The hydrotrope solubilizer maintains the rinse composition in a single phase solution having the nonionic rinsing agent uniformly  
25      distributed throughout the composition.

Preferred hydrotrope solubilizers are used at about 0.1 to 20 wt-% and include small molecule anionic surfactants. The most preferred hydrotrope solubilizers are used at about 1 to 10 wt-% and include aromatic  
30      sulfonic acid or sulfonated hydrotropes such as C<sub>1-5</sub> substituted benzene sulfonic acid or naphthalene sulfonic acid. Examples of such a hydrotrope are xylene sulfonic acid or naphthalene sulfonic acid or salts thereof. Such materials do not provide any pronounced  
35      surfactant or sheeting activity but significantly improve the solubility of the organic materials of the rinse aid in the aqueous rinse compositions.

Thus, a preferred embodiment of a rinse aid composition for plasticware, which is suitable for dilution to form an aqueous rinse includes: (a) about 2 to 90 wt-% of one or more nonionic surfactants; 5 (b) about 1 to 20 wt-% of a hydrotrope; (c) about 0.1 to 10 wt-% of a polysiloxane copolymer of the formula



wherein R is  $-(\text{CH}_2)_3-\text{O}-(\text{EO})_x-(\text{PO})_y-\text{Z}$  or



15 n is 0 or 1; m is at least 1, Z is hydrogen or alkyl of 1-6 carbon atoms, and the weight ratio in % of EO:PO may vary from 100:0 to 0:100, and, optionally, (d) about 0.1 to 10 wt-% of an ethoxylated fluoroaliphatic sulfonamide alcohol.

20 Another embodiment of the rinse aid composition of the present invention is the above-described siloxane surfactant with a rinse aid composition containing a nonionic block copolymer and a defoamer composition, and, optionally, in combination 25 with the above-described fluorocarbon surfactant. The nonionic ethylene oxide propylene oxide block copolymer in this case would not have been expected to provide effective sheeting action and low foam in an aqueous rinse due to its high cloud point and poor wetting 30 properties. However, rinse agents diluted into an aqueous rinse providing effective sheeting and low foaming properties have been prepared from high cloud point, high foaming surfactants with an appropriate

defoamer as described in copending U.S. application Serial No. 08/049,973 of April 20, 1993.

Illustrative but non-limiting examples of various suitable high cloud point nonionic surface 5 active agents for these rinse agents include polyoxyethylene-polyoxypropylene block copolymers having the formula:



wherein x, y and z reflect the average molecular

10 proportion of each alkylene oxide monomer in the overall block copolymer composition. x typically ranges from about 30 to 130, y typically ranges from about 30 to 70, z typically ranges from about 30 to 130, and x plus y is typically greater than about 60. The total 15 polyoxyethylene component of the block copolymer constitutes typically at least about 40 mol-% of the block copolymer and commonly 75 mol-% or more of the block copolymer. The material preferably has a molecular weight greater than about 5,000 and more 20 preferably greater than about 10,000.

Defoaming agents (defoamers) include a variety of different materials adapted for defoaming a variety of compositions. Defoamers can comprise an anionic or nonionic material such as polyethylene glycol,

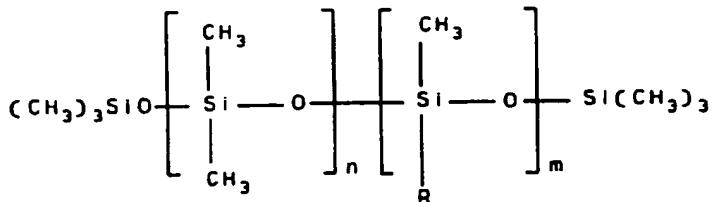
25 polypropylene glycol, fatty acids and fatty acid derivatives, fatty acid sulfates, phosphate esters, sulfonated materials, silicone based compositions, and others.

Preferred defoamers are food additive 30 defoamers including silicones and other types of active anti-foam agents.

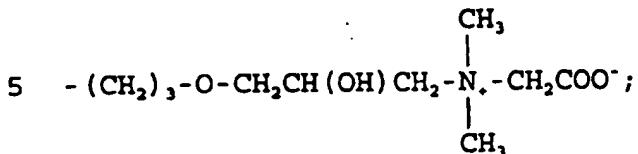
Silicone foam suppressors include polydialkylsiloxane preferably polydimethylsiloxane. Such silicone based foam suppressors can be combined 35 with silica. Such silica materials can include silica, fumed silica, derivatized silica, silanated silica, etc. Commonly available anti-foaming agents combine a

polydimethylsiloxane and silica gel. Another food additive defoaming agent comprises a fatty acid defoamer. Such defoamer compositions can comprise simple alkali metal or alkaline earth metal salts of a 5 fatty acid or fatty acid derivatives. Examples of such derivatives include mono, di- and tri- fatty acid esters of polyhydroxy compounds such as ethylene glycol, glycerine, propylene glycol, hexylene glycol, etc. Preferably such defoaming agents comprise a fatty acid 10 monoester of glycerol. Fatty acids useful in such defoaming compositions can include any C<sub>8-24</sub> saturated or unsaturated, branched or unbranched mono or polymeric fatty acid and salts thereof, including for example myristic acid, palmitic acid, stearic acid, behenic 15 acid, lignoceric acid, palmitoleic acid, oleic acid, linoleic acid, arachidonic acid, and others commonly available. Other food additive anti-foam agents available include water insoluble waxes, preferably microcrystalline wax, petroleum wax, synthetic petroleum 20 wax, rice base wax, beeswax having a melting point in the range from about 35° to 125°C with a low saponification value, white oils, etc. Such materials are used in the rinse agents at a sufficient concentration to prevent the accumulation of any 25 measurable stable foam within the dish machine during a rinse cycle. The defoaming composition may be present in the composition of the present invention from about 0.1-30 wt-%, preferably 0.2-25 wt-%.

Thus, a preferred rinse aid composition for 30 plasticware, suitable for dilution to form an aqueous rinse also includes: (a) about 5 to 40 wt-% of a nonionic block copolymer composition of ethylene oxide and propylene oxide, having a molecular weight of  $\approx$  5000 and a cloud point, measured with a 1 wt-% aqueous 35 solution, greater than 50°C; (b) about 0.2 to 25 wt-% of a food additive defoamer composition; (c) about 0.1 to 10 wt-% of a polysiloxane copolymer of the formula



wherein R is  $-(\text{CH}_2)_x-\text{O}-(\text{EO})_y-(\text{PO})_z-\text{Z}$  or



n is 0 or 1; m is at least 1, Z is hydrogen or alkyl of 10 1-6 carbon atoms, and the weight ratio in % of EO:PO may vary from 100:0 to 0:100, and, optionally, (d) about 0.1 to 10 wt-% of an ethoxylated fluoroaliphatic sulfonamide alcohol.

Still another embodiment of the present 15 invention is a rinse aid composition containing the above-described siloxane surfactant with a rinse aid composition containing solely food additive ingredients and, optionally, in combination with the above-described fluorocarbon surfactant. The compositions include a 20 class of nonionic surfactants, namely, the polyalkylene oxide derivatives of sorbitan fatty acid esters, which exhibit surprising levels of sheeting action, with a careful selection of defoamer compositions. These are described in copending U.S. Application Serial 25 No. 08/050,531 of April 20, 1993. The effective defoamer compositions are selected from the group consisting of a silicone defoamer, an alkali metal (e.g. sodium, potassium, etc.) or alkaline earth fatty acid salt defoamer or a glycerol fatty acid monoester 30 defoamer described above. Preferably, silicone based materials are used to defoam the sorbitan material.

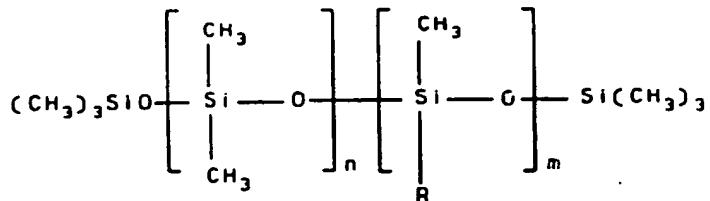
Sorbitol and sorbitan can be derivatized with an alkylene oxide such as ethylene oxide or propylene

oxide or derivatized with fatty acids or with both using conventional technology to produce nonionic surfactant sheeting agent materials. These sheeting agents are typically characterized by the presence of from 1 to 5 3 moles of a fatty acid, in ester form, per mole of surfactant and greater than 15 moles of alkylene oxide, preferably 15 to 40 moles of alkylene oxide and most preferably 15 to 25 moles of ethylene oxide per mole of surfactant. The composition of the surfactant is a 10 mixture of a large number of compounds characterized by the molar proportion of alkylene oxide and the molar proportion of fatty acid residues on the sorbitol or sorbitan molecules. The compositions are typically characterized by average concentrations of the alkylene 15 oxide (typically ethylene oxide) and the fatty acid on the overall compositions. Examples of preferred nonionic surfactants are Polysorbate 20<sup>®</sup>, also known as Tween 20<sup>®</sup> (ICI), typically considered to be a mixture of laureate esters of sorbitol and sorbitan consisting 20 predominantly of the mono fatty acid ester condensed with approximately 20 moles of ethylene oxide. Polysorbate 60<sup>®</sup> is a mixture of stearate esters of sorbitol and sorbitan consisting predominantly of the mono fatty acid ester condensed with approximately 20 25 moles of ethylene oxide. Selected polysorbate nonionic surfactant materials are approved for direct use in food intended for human consumption under specified conditions and levels of use.

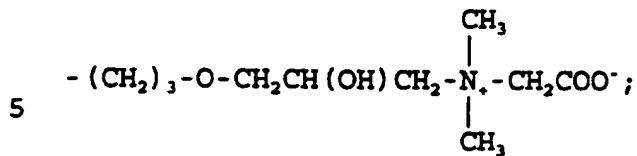
Alkoxylated sorbitan or sorbitol aliphatic 30 esters suitable for use in the rinse aid composition include any sorbitan or sorbitol aliphatic ester derivatized with an alkylene oxide capable of providing effective sheeting action or rinsing performance in cooperation with the other components of the rinse agent 35 composition. The preferred compositions are the ethylene oxide condensates with sorbitan or sorbitol fatty acid esters. In addition to providing superior

sheeting and rinsing performance, these materials are approved food additives, in the form of a liquid or waxy solid, that can be easily formulated into concentrated liquid or solid rinse agents. Alkoxylated sorbitan or 5 sorbitol fatty acid esters suitable for use in the rinse agent include mono, di- and tri-esters and mixtures thereof. Sorbitan fatty acid esters may be derivatized by esterification of sorbitol or sorbitan with such fatty acids as lauric, myristic, palmitic, stearic, 10 oleic, linoleic, and other well known similar saturated, unsaturated (cis or trans), branched and unbranched fatty acid. Preferred food additive or GRAS fatty acids are the sorbitan esters approved as direct food additives (e.g. sorbitan monostearate, POE 20 Sorbitan 15 monolaurate, POE 20 Sorbitan monostearate, POE 20 Sorbitan tristearate, POE 20 Sorbitan monooleate and mixtures thereof. Based on their cost availability and ability to provide excellent sheeting action and rinsing performance, the preferred useful ethoxylated sorbitan 20 or sorbitol fatty acid ester include monoesters derivatized with ethylene oxide.

Thus, a preferred rinse aid composition for plasticware, suitable for dilution to form an aqueous rinse, further includes: (a) about 5 to 50 wt-% of a 25 sorbitan fatty acid ester containing greater than about 15 moles of alkylene oxide per mole of sorbitan; (b) about 0.2 to 25 wt-% of a defoamer composition selected from the group consisting of an alkali metal or alkaline earth metal salt of a fatty acid, a silicone, a fatty 30 acid ester of glycerol, and mixtures thereof; (c) about 0.1 to 10 wt-% of a polysiloxane copolymer of the formula



wherein R is  $-(\text{CH}_2)_3-\text{O}-(\text{EO})_x-(\text{PO})_y-\text{Z}$  or



n is 0 or 1; m is at least 1, Z is hydrogen or alkyl of 1-6 carbon atoms, and the weight ratio in % of EO:PO may 10 vary from 100:0 to 0:100, and, optionally, (d) about 0.1 to 10 wt-% of an ethoxylated fluoroaliphatic sulfonamide alcohol.

The rinse agents of the invention can, if desired, contain a polyvalent metal complexing or 15 chelating agent that aids in reducing the harmful effects of hardness components in service water. Typically calcium, magnesium, iron, manganese, etc., ions present in service water can interfere with the action of either washing compositions or rinsing 20 compositions. A chelating agent can effectively complex and remove such ions from inappropriate interaction with active ingredients increasing rinse agent performance. Both organic and inorganic chelating agents are common. Inorganic chelating agents include such compounds as 25 sodium tripolyphosphate and higher linear and cyclic polyphosphate species. Organic chelating agents include both polymeric and small molecule chelating agents. Polymeric chelating agents commonly comprise polyanionic compositions such as polyacrylic acid compounds. Small 30 molecule organic chelating agents include salts of ethylenediaminetetraacetic acid and hydroxyethylenediaminetetraacetic acid, nitrilotriacetic acid, ethylenediaminetetrapropionates, triethylenetetraminehexacetates, and the respective 35 alkali metal ammonium and substituted ammonium salts thereof. Amino phosphates are also suitable for use as chelating agents in the composition of the invention and include ethylenediamine(tetramethylene phosphates), nitrilotrismethylene phosphonates, diethylenetriamine

(pentamethylenephosphonates). These amino phosphonates commonly contain alkyl or alkyl groups with less than 8 carbon atoms. Preferred chelating agents include approved food additive chelating agents such as disodium 5 salt of ethylenediaminetetraacetic acid.

The liquid rinse agent compositions of the invention have a liquid base component which can function as a carrier with various aqueous diluents to form the aqueous rinse. Liquid bases are preferably 10 water or a solvent compatible with water to obtain compatible mixtures thereof. Exemplary nonlimiting solvents in addition to water include low molecular weight C<sub>1-6</sub> primary and secondary mono, di-, and trihydrate alcohol such as ethanol, isopropanol, and 15 polyols containing from two to six carbon atoms and from two to six hydroxyl groups such as propylene glycol, glycerine, 1,3-propane diol, propylene glycol, etc.

The compositions of the invention can be formulated using conventional formulating equipment and 20 techniques. The compositions of the invention typically can comprise proportions as set forth in Table I.

In the manufacture of the liquid rinse agent of the invention, typically the materials are manufactured in commonly available mixing equipment by 25 charging to a mixing chamber the liquid diluent or a substantial proportion of a liquid diluent. Into a liquid diluent is added preservatives or other stabilizers. Care must be taken in agitating the rinse agent as the formulation is completed to avoid 30 degradation of polymer molecular weight or exposure of the composition to elevated temperatures. The materials are typically agitated until uniform and then packaged in commonly available packaging and sent to storage before distribution.

35 The liquid materials of the invention can be adapted to a solid block rinse by incorporating into the composition a casting agent. Typically organic and

inorganic solidifying materials can be used to render the composition solid. Preferably organic materials are used because inorganic compositions tend to promote spotting in a rinse cycle. The most preferred casting 5 agents are polyethylene glycol and an inclusion complex comprising urea and a nonionic polyethylene or polypropylene oxide polymer. Polyethylene glycols (PEG) are used in melt type solidification processing by uniformly blending the sheeting agent and other 10 components with PEG at a temperature above the melting point of the PEG and cooling the uniform mixture. An inclusion complex solidifying scheme is set forth in Morganson et al., U.S. Patent No. 4,647,258.

The organic nature of the rinse agents of the 15 invention can be subject to decomposition and microbial attack. Preferred stabilizers that can limit oxidative decomposition or microbial attack include food grade stabilizers, food grade antioxidants, etc. Most preferred materials for use in stabilizing the 20 compositions of the invention include C<sub>1-10</sub> mono, di- and tricarboxylic acid compounds. Preferred examples of such acids include acetic acid, citric acid, lactic, tartaric, malic, fumaric, sorbic, benzoic, etc.

Optional ingredients which can be included in 25 the rinse agents of the invention in conventional levels for use include solvents, processing aids, corrosion inhibitors, dyes, fillers, optical brighteners, germicides, pH adjusting agents (monoethanol amine, sodium carbonate, sodium hydroxide, hydrochloride acid, 30 phosphoric acid, etc.), bleaches, bleach activators, perfumes and the like.

The range of actives in the solid and liquid 35 concentrate compositions of the invention are set forth in Table I and the ranges in the aqueous rinse in Table II.

TABLE I

	<u>Actives (wt-%)</u>	<u>Useful (wt-%)</u>	<u>Preferred</u>
	<u>Solid</u>	<u>Liquid</u>	
5	Hydrocarbon surfactant	2-90	8-305-75
10	Fluorocarbon surfactant	0.1-10	0.5-50.5-5
	Siloxane surfactant	0.1-10	0.5-50.5-5

15

TABLE II

	<u>Actives (ppm)</u>	<u>Useful (ppm)</u>	<u>Preferred</u>
20	Hydrocarbon surfactant	2-100	30-50
	Fluorocarbon surfactant	0.01-10	0.1-1.0
25	Siloxane surfactant	0.01-10	0.1-1.0

25                   Liquid rinse agents of the invention are typically dispensed by incorporating compatible packaging containing the liquid material into a dispenser adapted to diluting the liquid with water to a 30 final use concentration wherein the active material is present in the aqueous rinse as shown in Table II above in parts per million parts of the aqueous rinse. Examples of dispensers for the liquid rinse agent of the invention are DRYMASTER-P sold by Ecolab Inc., St. Paul, 35 Minnesota.

35                   Solid block products may be conveniently dispensed by inserting a solid block material in a container or with no enclosure into a spray-type dispenser such as the volume SOL-ET controlled ECOTEMP 40 Rinse Injection Cylinder system manufactured by Ecolab Inc., St. Paul, Minnesota. Such a dispenser cooperates with a warewashing machine in the rinse cycle. When demanded by the machine, the dispenser directs a spray of water onto the solid block of rinse agent which 45 effectively dissolves a portion of the block creating a concentrated aqueous rinse solution which is then fed

directly into the rinse water forming the aqueous rinse. The aqueous rinse is then contacted with the dishes to affect a complete rinse. This dispenser and other similar dispensers are capable of controlling the 5 effective concentration of the active block copolymer and the additives in the aqueous rinse by measuring the volume of material dispensed, the actual concentration of the material in the rinse water (an electrolyte measured with an electrode) or by measuring the time of 10 the spray on the solid block.

The following examples and data further illustrate the practice of the invention. These should not be taken as limiting the invention and contain the best mode.

15

EXAMPLE I

The following four liquid formulations were prepared by routine mixing of the ingredients.

20	Item	Raw Material	Formula No. (wt. %)			
			1	2	3	4
	1	EO/PO Block Terminated with PO (32% EO)	19.300	19.720	19.633	19.461
	2	EO/PO Block Terminated with PO (39% EO)	52.309	54.147	53.908	53.436
	3	Fluorad™ FC-170C		0.887		0.875
	4	® Silwet L-77*			1.325	1.313
25	5	C <sub>14-15</sub> linear primary alcohol ethoxylate	5.000	5.067	5.044	5.000
	6	Inerts to 100%				

\* Siloxane of the formula described above where Z is methyl, n is 0, m is 1 and the weight ratio in % of EO:PO is 100:0.

These formulations were evaluated in a modified Champion 1 KAB dishwash machine modified to replace the front stainless panel with a glass window 35 and to conduct rinsing tests using the machine pump and wash arms.

The test procedure is first to select appropriate test substrates to evaluate the test formulations. These substrates are typical pieces of plasticware commonly used in institutional accounts. In 5 preparation for the sheeting test, the test substrates are conditioned with 0.2% Hotpoint soil in softened water at 160°F for three minutes in the modified Champion 1 KAB dishmachine. The test procedure is to add test rinse aid in increments of 10 ppm actives, to 10 the machine pump, circulate the test solution at 160°F for 30 seconds, turn off the machine and observe the type of water break on each test substrate. There are three types of water break. These are:

0. No Sheeting. The test solution runs off 15 the test substrate leaving discrete droplets behind.

1. Pinhole Sheeting. The test solution drains off of the test substrate to leave a continuous film. The film contains pinholes on the surface of the film. No droplets remain on the test substrate after 20 the film drains and dries.

2. Complete Sheeting. The test solution drains off the test substrate to leave a continuous film with no pinholes. No droplets remain on the test substrate after the film drains and dries.

25 The type of water used in this test is softened well water. After each evaluation of test rinse aid per 10 ppm active increment, the results are recorded for each test substrate. The test continues until a good performance profile is obtained that allows 30 a judgment to be made regarding the relative performance of the test formulations.

Results are given below in table form for each of the four formulations noted above.

35 Tables 1-4

Table 1 contains results for a commercially available rinse aid. Note that none of the plastic

substrates exhibit complete sheeting until 70 ppm actives are used.

Table 2 contains results for the same set of actives containing Fluorad™ FC-170C. It performs 5 marginally better at 60 ppm to complete sheet on some of the plastic substrates.

Table 3 contains results for the same set of actives containing Silwet® L-77. It also performs marginally better at 60 ppm to complete sheet on some of 10 the plastic substrates.

Table 4 contains results for the invention. This contains both Silwet® L-77 and Fluorad™ FC-170C. It performs much better at 40 ppm to complete sheet on several of the plastic substrates.

15 The invention represented as Formulation 4 was also evaluated in four institutional test accounts relative to the commercially available rinse aid represented as Formulation 1. In each account at either the same or even at a lower concentration, there has 20 been a significant improvement in drying results on plasticware. With the commercially available product large residual droplets of rinse water remained on the plasticware so that the dry time was much too long, i.e., the plasticware was stacked wet. With the 25 invention, the dry time was greatly reduced and the plasticware was stacked dry.

TABLE I  
Follett 21

Soft water, 160°F, Hotpoint Soiled Dishes. (-) no sheeting, ( ) pinhole sheeting, (X) complete sheeting.

TABLE 2  
Formula 2

5      Formula 1 with FC-170-C and no Silwet® L-77  
soft water, 160°F, Hotpoint Soiled Dishes. (-) no sheeting, (|) pinhole sheeting,  
(X) complete sheeting.

	Parts Per Million Actives	0	10	20	30	40	50	60	70	80	90	100
PC Bowl	-	-	-	-	-	-	-	-	-	-	-	X
PC Tile	-	-	-	-	-	-	-	-	-	-	-	X
Glass	-	-	-	-	-	-	-	X	X	X	X	X
China Plate	-	-	-	-	-	-	-	X	X	X	X	X
Mel Plate	-	-	-	-	-	-	-	X	X	X	X	X
P3 Plate	-	-	-	-	-	-	-	X	X	X	X	X
P3 Cup	-	-	-	-	-	-	-	X	X	X	X	X
Dnx Cup	-	-	-	-	-	-	-	X	X	X	X	X
Dnx Bowl	-	-	-	-	-	-	-	X	X	X	X	X
P3 Jug	-	-	-	-	-	-	-	X	X	X	X	X
Poly Try	-	-	-	-	-	-	-	X	X	X	X	X
PS (dish)	-	-	-	-	-	-	-	X	X	X	X	X
PS Spoon	-	-	-	-	-	-	-	X	X	X	X	X
SS Knife	-	-	-	-	-	-	-	X	X	X	X	X
Temp °F	160	160	160	160	160	160	160	160	160	160	160	160
Foam "	0	0	0	0	0	0	0	0	0	0	0	0

TABLE 3  
Formula 3

5 Formula 1 with Silwet® L-77 and no FC-170-C  
soft water, 160°F. Hotpoint Soiled Dishes. (-) no sheeting, (||) pinhole sheeting.  
(X) complete sheeting.

	Parts Per Million	0	10	20	30	40	50	60	70	80	90	100
Actives												
PC Bowl	-	-	-	-	-	-	-	-	X	X	X	
PC Tile	-	-	-	-	-	-	-	-	-	-	-	
Glass	-	-	-	-	-	-	-	X	X	X	X	
China Plate	-	-	-	-	-	-	-	-	X	X	X	
Mel Plate	-	-	-	-	-	-	-	-	X	X	X	
P3 Plate	-	-	-	-	-	-	-	-	X	X	X	
P3 Cup	-	-	-	-	-	-	-	X	X	X	X	
Dnx Cup	-	-	-	-	-	-	X	X	X	X	X	
Dnx Bowl	-	-	-	-	-	-	X	X	X	X	X	
P3 Jug	-	-	-	-	-	-	-	-	-	-	-	
Poly Try	-	-	-	-	-	-	-	X	X	X	X	
PS (dish)	-	-	-	-	-	-	-	-	-	-	-	
PS Spoon	-	-	-	-	-	-	-	-	X	X	X	
SS Knife	-	-	-	-	-	-	-	-	X	X	X	
Temp °F	160	160	160	159	160	160	160	160	160	160	161	161
Foam "	0	0	0	0	0	0	0.3	0.3	0.4	0.6	0.8	0.9

TABLE 4  
Formula 4

5 Formula 1 with Silwet<sup>®</sup> L-77 and FC-170C.

10 Soft water, 160°F, Hotpoint Soiled Dishes. (-) no sheeting, (|) pinhole sheeting, (X) complete sheeting.

	Parts Per Million Actives	0	10	20	30	40	50	60	70	80	90	100
PC Bowl	-	-	-	-	X	X	X	X	X	X	X	
PC Tile	-	-	-	-	-	X	X	X	X	X	X	
Glass	-	-	-	-	X	X	X	X	X	X	X	
China Plate	-				X	X	X	X	X	X	X	
MeI Plate	-	-	-	-	X	X	X	X	X	X	X	
P3 Plate	-	-	-	-	-	X	X	X	X	X	X	
P3 Cup	-	-	-	-	X	X	X	X	X	X	X	
Dnx Cup	-	-	-	-	X	X	X	X	X	X	X	
Dnx Bowl	-	-	-	-	X	X	X	X	X	X	X	
P3 Jug	-	-	-	-	-	X	X	X	X	X	X	
Poly Try	-	-	-	-	X	X	X	X	X	X	X	
PS (dish)	-	-	-	-	-	X	X	X	X	X	X	
PS Spoon	-	-	-	-	-	X	X	X	X	X	X	
SS Knife	-	-	-	-	X	X	X	X	X	X	X	
Temp °F	160	160	160	160	161	161	158	160	161			
Foam "	0	0	0	0	0	0.1	0.2	0.4	0.3	0.2		

EXAMPLE II

The following three solid rinse aid formulations were prepared as previously described and compared side by side. Formula 5 contained the same active ingredients as Formula 4 of Example I. The results (Tables 5, 6 and 7) show similar effectiveness as with the Formula 4 compositions.

Item	Raw Material	Formula No. (wt-%)
		5
		6
		7
1	EO/PO Block Terminated with PO (32% EO)	19.649
2	EO/PO Block Terminated with PO (39% EO)	53.248
10	3 Fluorad™ FC-170C	0.875
4	Silvet® L-77	1.313
5	ABIL® -B-8852 <sup>(a)</sup>	1.313
6	ABIL® -B-8863 <sup>(b)</sup>	1.313
15	7 C <sub>4-13</sub> linear primary alcohol ethoxylate	5.000
8	8 Urea	16.000
9	9 Inerts to 100%	16.000

(a) A siloxane of the formula described above where Z is H and the EO:PO weight ratio in % is 20:80.

(b) A siloxane of the formula described above where Z is H and the EO:PO weight ratio in % is 40:60.

TABLE 5  
Formula 5

	Parts Per Million	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150
5	Polycarbonate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Tile																
	Polycarbonate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Bowl																
10	Glass Tumbler	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	China Plate																
	Melamine Plate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Polypropylene	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Plate																
15	Polypropylene Cup	-	-	-	-	-	-	-	x	x	x	x	x	x	x	x	x
	Dinex Cup								x	x	x	x	x	x	x	x	x
	Dinex Bowl								x	x	x	x	x	x	x	x	x
	Polypropylene Jug	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Poly Tray	-	-	-	-	-	-	-	x	x	x	x	x	x	x	x	x
20	Polysulfonate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Dish																
	Polysulfonate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Spoon																
	Stainless Steel	-	-	-	-	-	-	-	-	x	x	x	x	x	x	x	x
25	Knife																
	Temperature (F)	161	161	161	161	160	160	160	160	160	160	160	160	160	160	160	160
	Foam (")	0	0	0	0	0	0	0	0	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.3

**TABLE 6**  
**Formula 6**

	Parts Per Million	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150
Polycarbonate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Tile	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polycarbonate Bowl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Glass Tumbler	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
China Plate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Melamine Plate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polypropylene Plate	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polypropylene Cup	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dinex Cup	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dinex Bowl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polypropylene Jug	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Poly Tray	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polysulfonate Dish	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Polysulfonate Spoon	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Stainless Steel Knife	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Temperature (F)	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160
Foam (%)	0	0	0	0	0	0	0	0	0	0	0.1	0.1	0.1	0.2	0.2	0.3	0.3

**TABLE 7**  
**Formula 7**

Parts Per Million	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150
<b>Polycarbonate</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Tile</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Polycarbonate Bowl</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Glass Tumbler</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>China Plate</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Melamine Plate</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Polypropylene Plate</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Polypropylene Cup</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>DineX Cup</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>DineX Bowl</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Polypropylene Jug</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Poly Tray</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Polyulfonate Dish</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Polyulfonate Spoon</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Stainless Steel Knife</b>	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
<b>Temperature (F)</b>	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160
<b>Foam (°)</b>	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

5

10

15

20

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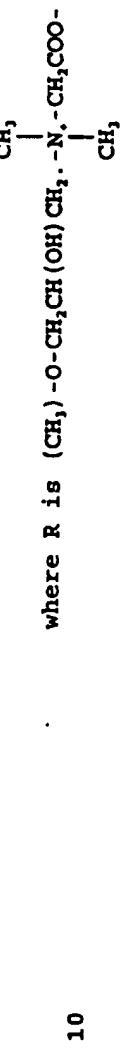
30

## EXAMPLE II

The following formulations were made and evaluated. All additives are used at the same concentration of actives.

5 ABIL QUAT 3272 is available from Goldschmidt Chemical and is a copolymer of polydimethyl siloxane and an organic quaternary nitrogen groups. It is 50% active.

5 ABIL B9550 is available from Goldschmidt Chemical and is a polysiloxane polyorganobetaine copolymer of the formula described above



15 ABIL B-8847 A silicone of the formula described above where Z is H and the EO:PO wt. ratio is 80:20 mwt. 800.

B-8842 A silicone of the formula described above where Z is H and the EO:PO wt. ratio is 100:0 mwt. 5,00.

B-8878 A silicone of the formula described above where Z is H and the EO:PO wt. ratio is 100:1 mwt. 600.

Tegopren 5840 Polyether polysiloxane

20 PECONSIL SPB-1240 are available from Phoenix Chemical and are  
and SMQ-40  
and CAP-1240  
Silicone Phosphobetaines. These are 40% active.

These formulations were evaluated in a modified Champion 1 KAB dishwash machine as described in Example I.

5 Results are given below in table form for each of the ten formulations noted above.

Tables 8-17

10 Table 8 contains results for a commercially available rinse aid. Note that none of the plastic substrates exhibit complete sheeting until 70 ppm actives are used. This is that standard formulation that the next nine are compared to.

15 Table 9 contains results for the same set of actives containing ABIL B-9950. It performs much better at 40 ppm to complete sheet on some of the plastic substrates. This formulation represents the invention.

20 Table 10 contains results for the same set of actives containing ABIL-Quat 3272. It performs marginally worse at 80 ppm to complete sheet on some of the plastic substrates.

25 Table 11 contains results for the same set of actives containing ABIL-B-8878. It performs marginally better at 60 ppm to complete sheet on some of the plastic substrates.

30 Table 12 contains results for the same set of actives containing ABIL-B-8847. It performs marginally better at 60 ppm to complete sheet on some of the plastic substrates.

35 Table 13 contains results for the same set of actives containing ABIL-B-8842. It performs at 50 ppm to complete sheet on some of the plastic substrates. This is a second embodiment of the invention.

40 Table 14 contains results for the same set of actives containing Tegopren-5840. It performs much worse with no complete sheeting on any plastic substrates up to 150 ppm.

45 Table 15 contains results for the same set of actives containing PECOSIL SMQ-40. It performs much worse with no complete sheeting on any plastic substrates up to 150 ppm.

5      Table 16 contains results for the same set of actives containing PECOSIL SPB-1240. It performs radically worse with no sheeting on any substrates up to 150 ppm.

10     Table 17 contains results for the same set of actives containing PECOSIL CAP-1240. It performs marginally worse at 90 ppm to complete sheet on some of the plastic substrates.

15     The nature of the silicone additive can radically affect results. Some additives provide much better results when added to the basic set of rinse aid ingredients, some do not affect results much, and some detract from results.

20     The invention represented as Formulation 9 was also evaluated in eight institutional test accounts relative to the commercially available rinse aid represented as Formulation 1. In each account at either the same or even at a lower concentration, there has been a significant improvement in drying results on plasticware. With the commercially available product large residual droplets of rinse water remained on the plasticware so that the dry time was much too long. With the invention either there were very small residual droplets of rinse water or the rinse water sheeted from the plasticware. The dry time was greatly reduced and results were judged as acceptable.

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**TABLE 8**

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TABLE 2

	Parts Per Million	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	175	200	225
Polycarbonate Tile	0	0	0	0	0	1	1	1	1	2	2	2	2	2	2	2	2	2	2	
Polycarbonate Bowl	0	0	0	0	0	1	1	1	2	2	2	2	2	2	2	2	2	2	2	
Glass Tumbler	0	0	0	0	0	0	1	1	2	2	2	2	2	2	2	2	2	2	2	
China Plate	0	0	0	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	
Melamine Plate	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Polypropylene Plate	0	0	0	1	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	
Polypropylene Cup	0	0	0	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
Dinex Cup	0	0	0	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
Dinex Bowl	0	0	0	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
Polypropylene Jug	0	0	0	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
Poly Tray	0	0	0	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
Polysulfonate Dish	0	0	0	0	0	1	1	2	2	2	2	2	2	2	2	2	2	2	2	
Polysulfonate Spoon	0	0	0	0	0	0	1	1	2	2	2	2	2	2	2	2	2	2	2	
Stainless Steel Knife	0	0	0	0	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	
Temperature (F)	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	

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TABLE 10

	Parts Per Million	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	175	200	225
5 Polycarbonate Tile	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	
5 Polycarbonate Bowl	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	
5 Glass Tumbler	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	
5 China Plate	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	
10 Melamine Plate	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	
10 Polypropylene Plate	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	
10 Polypropylene Cup	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	2	2	2	
10 Dinex Cup	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	2	2	2	
10 Dinex Bowl	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	2	2	2	
15 Polycarbonate Jug	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	
15 Poly Tray	0	0	0	1	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2	
15 Polysulfonate Dish	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	
15 Polysulfonate Spoon	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	
20 Stainless Steel Knife	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	
20 Temperature (F)	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	

TABLE 11

	Parts Per Million	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	175	200	225
5	<b>Polycarbonate</b>	0	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	2	
10	<b>Polycarbonate</b>	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	
15	<b>Glass</b>	0	0	0	0	0	0	0	0	1	1	1	1	2	2	2	2	2	2	
20	<b>China</b>	0	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	2	
25	<b>Melamine</b>	0	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	2	
30	<b>Polypolyethylene</b>	0	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	2	
35	<b>Polypolyethylene</b>	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	
40	<b>Cup</b>	0	0	0	0	0	0	0	1	1	1	1	2	2	2	2	2	2	2	
45	<b>Dinex</b>	0	0	0	0	0	0	0	1	1	1	1	2	2	2	2	2	2	2	
50	<b>Bowl</b>	0	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	2	
55	<b>Polypropylene</b>	0	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	2	
60	<b>Jug</b>	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	
65	<b>Poly</b>	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	
70	<b>Tray</b>	0	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	2	
75	<b>Polyulfonate</b>	0	0	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	
80	<b>Dish</b>	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	
85	<b>Polysulfonate</b>	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	
90	<b>Spoon</b>	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	
95	<b>Stainless Steel</b>	0	0	0	0	0	0	0	0	0	1	1	1	2	2	2	2	2	2	
100	<b>Knife</b>	0	0	0	0	0	0	0	0	0	0	1	1	2	2	2	2	2	2	
105	<b>Temperature (F)</b>	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	

TABLE 12

	Parts Per Million	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	175	200	225
Polycarbonate Tie	0	0	0	0	0	1	1	2	2	2	2	2	2	2	2	2	2	2	2	
Polycarbonate Bowl	0	0	0	0	0	1	1	1	2	2	2	2	2	2	2	2	2	2	2	
Glass Tumbler	0	0	0	0	0	1	1	1	1	1	1	2	2	2	2	2	2	2	2	
China Plate	0	0	0	0	0	0	1	2	2	2	2	2	2	2	2	2	2	2	2	
Melamine Plate	0	0	0	0	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	
Polypropylene Plate	0	0	0	0	1	1	1	1	2	2	2	2	2	2	2	2	2	2	2	
Polypropylene Cup	0	0	0	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	
Dinex Cup	0	0	0	0	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	
Dinex Bowl	0	0	0	0	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	
Polypropylene Jug	0	0	0	0	0	0	1	1	1	1	1	2	2	2	2	2	2	2	2	
Poly Tray	0	0	0	1	1	1	2	2	2	2	2	2	2	2	2	2	2	2	2	
Polysulfonate Dish	0	0	0	0	0	0	1	1	1	2	2	2	2	2	2	2	2	2	2	
Polysulfonate Spoon	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	
Stainless Steel Knife	0	0	0	0	0	1	2	2	2	2	2	2	2	2	2	2	2	2	2	
Temperature (F)	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	

TABLE 13

TABLE 14

TABLE 15

	Parts Per Million	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	175	200	225
Polycarbonate Tile	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1
Polycarbonate Bowl	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1
Glass Tumbler	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1
China Plate	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Melamine Plate	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1
Polypropylene Plate	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Polypropylene Cup	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1
Dinex Cup	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1
Dinex Bowl	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1
Polypropylene Jug	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1
Poly Tray	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1	1
Polysulfonate Dish	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1
Polysulfonate Spoon	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1
Stainless Steel Knife	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1
Temperature (F)	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	

**TABLE 16**

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TABLE 17

Parts Per Million	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	175	200	225
Polycarbonate Tile	0	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1
Polycarbonate Bowl	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Glass Tumbler	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
China Plate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Melamine Plate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Polypropylene Plate	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1
Polypropylene Cup	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1
Dinex Cup	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1	1
Dinex Bowl	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1	1
Polypropylene Jug	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1	1
Poly Tray	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	1
Polyulfonate Dish	0	0	0	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1
Polyulfonate Spoon	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Stainless Steel Knives	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Temperature (°F)	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160

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#### EXAMPLE IV

The following formulations were made and evaluated. All additions are used at the same concentration of actives.

**TABLE 18**

**TABLE 19**

**TABLE 20**

TABLE 21

TABLE 22



**TABLE 24**

TABLE 25  
Characteristics of Nonionic Polydimethylsiloxane Polymers and Test Results

Product	Resin No.								
Silwet L-77	ALL EO	Me	600						60*
Silwet L-720	50/50	Bu	12000						50*
Silwet L-7001	40/60	Me	20000						70*
Silwet L-7200	75/25	H	19000						60*
Silwet L-7230	40/60	H	29000						60*
Silwet L-7602	ALL EO	Me	3000						70*
Silwet L-7604	ALL EO	H	4000						80*
Silwet L-7622	ALL EO	Me	10000						90*
ABIL-B-8878	ALL EO	H	600						60*
ABIL-B-8847	80/20	H	800						60*
ABIL-B-8842	60/40	H	950						50*

\* Concentration of rinse aid required for initial complete sheeting of a plastic substrat

TABLE 26

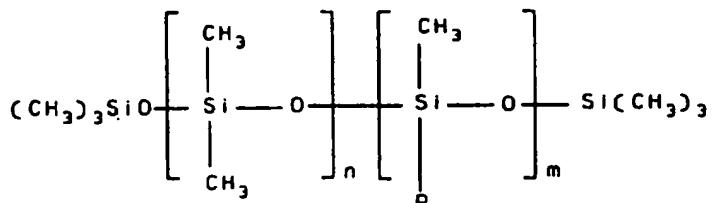
A Key to the Dishware Substrates used for the Plastic Rinse Additive Sheetng Test

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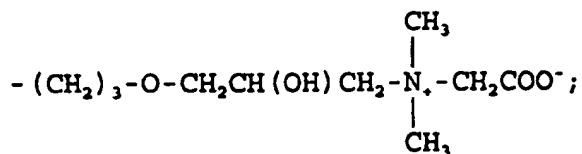
	<b>Abbreviated Title</b>	<b>Type of Dishware</b>
	PC Tile	Polycarbonate Tile
	PC Bowl	Polycarbonate Bowl
	Glass	Glass Tumbler
10	China Plt	China Plate
	Mel Plt	Melamine Plate
	P3 Plt	Polypropylene Plate
	P3 Plt	Polypropylene Cup
	Dnx Cup	Filled Polypropylene Cup
15	Dnx Bowl	Filled Polypropylene Bowl
	P3 Jug	Polypropylene Jug
	Poly Try	Polyester Resin Tray
	PS (dish)	Polysulfone Dish
	PS Spoon	Polysulfone Spoon
20	SS Knife	Stainless Steel Knife

WHAT IS CLAIMED IS:

1. A rinse aid composition for plasticware, suitable for dilution to form an aqueous rinse, comprising from about 0.1 to about 10 wt-% of a polysiloxane copolymer of the formula

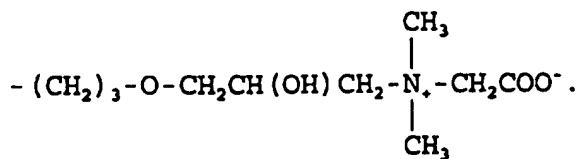


wherein R is  $-(CH_2)_3-O-(EO)_x-(PO)_y-Z$  or



n is 0 or 1; m is at least 1, Z is hydrogen or alkyl of 1-6 carbon atoms, and the weight ratio in % of EO:PO may vary from 100:0 to 0:100, in admixture with hydrocarbon surfactants.

2. The composition of claim 1, wherein R is



3. The composition of claim 1, wherein R is  $-(CH_2)_3-O-(EO)_x-(PO)_y-Z$ , in which Z is hydrogen, methyl or butyl and the weight ratio in % of EO to PO is 100:0 to 40:60.

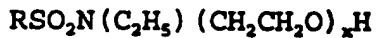
4. The composition of claim 1, wherein the hydrocarbon surfactants comprise one or more nonionic surfactants.

5. The composition of claim 4, wherein the nonionic surfactant is a block copolymer of polyethylene oxide and polypropylene oxide.

6. The composition of claim 3, which further comprises about 0.1 to about 10 wt-% of a fluorinated hydrocarbon surfactant.

7. The composition of claim 6, wherein the fluorinated hydrocarbon surfactant is an ethoxylated fluoroaliphatic sulfonamide alcohol, a fluoroaliphatic polyoxyethylene ethanol, a fluoroaliphatic alkoxylate or a fluoroaliphatic ester.

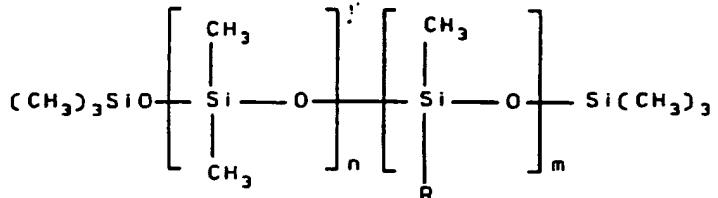
8. The composition of claim 7, wherein the ethoxylated fluoroaliphatic sulfonamide alcohol is of the formula



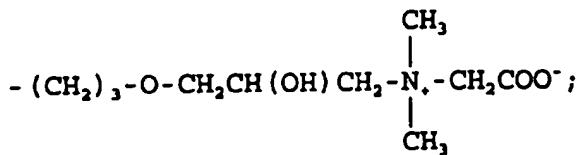
wherein R is  $C_nF_{2n+1}$  in which n is 6 to 10 and x may vary from 10 to 20.

9. A rinse aid composition for plasticware, suitable for dilution to form an aqueous rinse, comprising:

- (a) about 2 to 90 wt-% of one or more nonionic surfactants;
- (b) about 1 to 20 wt-% of a hydrotrope;
- (c) about 0.1 to 10 wt-% of a polysiloxane copolymer of the formula



wherein R is  $-(CH_2)_3-O-(EO)_x-(PO)_y-Z$  or



n is 0 or 1; m is at least 1, Z is hydrogen or alkyl of 1-6 carbon atoms, and the weight ratio in % of EO:PO may vary from 100:0 to 0:100.

10. The composition of claim 9, wherein R is  $-(\text{CH}_2)_3 - \text{O} - (\text{EO})_x - (\text{PO})_y - \text{Z}$ , in which Z is hydrogen, methyl or butyl and the weight ratio in % of EO to PO is 100:0 to 40:60.

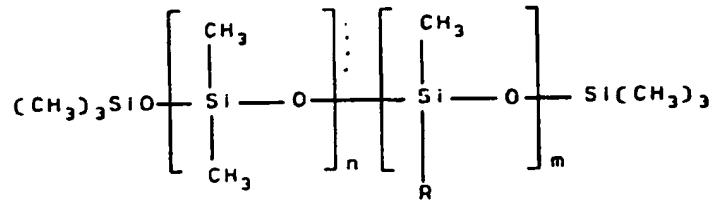
11. The composition of claim 10, which further comprises about 0.1 to 10 wt-% of an ethoxylated fluoroaliphatic sulfonamide alcohol.

12. A rinse aid composition for plasticware, suitable for dilution to form an aqueous rinse, the composition comprising:

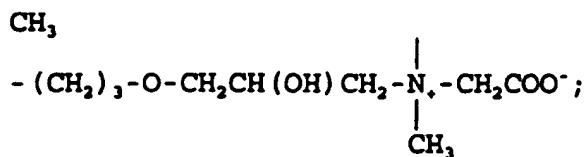
(a) about 5 to 40 wt-% of a nonionic block copolymer of ethylene oxide and propylene oxide, having a molecular weight of  $\geq 5000$  and a cloud point, measured with a 1 wt-% aqueous solution, greater than 50°C;

(b) about 0.2 to 25 wt-% of a food additive defoamer composition; and

(c) about 0.1 to 10 wt-% of a polysiloxane copolymer of the formula



wherein R is  $-(\text{CH}_2)_3 - \text{O} - (\text{EO})_x - (\text{PO})_y - \text{Z}$  or



n is 0 or 1; m is at least 1, Z is hydrogen or alkyl of 1-6 carbon atoms, and the weight ratio in % of EO:PO may vary from 100:0 to 0:100.

13. The composition of claim 12, wherein R is  $-(\text{CH}_2)_3 - \text{O} - (\text{EO})_x - (\text{PO})_y - \text{Z}$ , in which Z is hydrogen, methyl or butyl and the weight ratio in % EO to PO is 100:0 to 40:60.

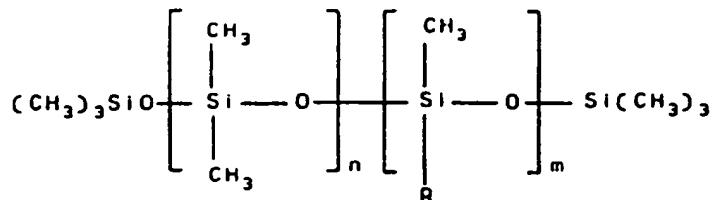
14. The composition of claim 13, which further comprises about 0.1 to 10 wt-% of an ethoxylated fluoroaliphatic sulfonamide alcohol.

15. A rinse aid composition for plasticware, suitable for dilution to form an aqueous rinse, the composition comprising:

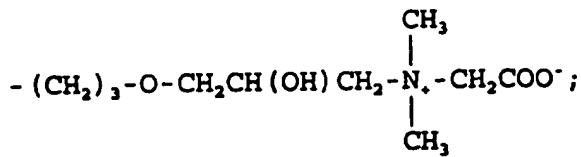
(a) about 5 to 50 wt-% of a sorbitan fatty acid ester containing greater than about 15 moles of alkylene oxide per mole of sorbitan;

(b) about 0.2 to 25 wt-% of a defoamer composition selected from the group consisting of an alkali metal or alkaline earth metal salt of a fatty acid, a silicone, a fatty acid ester of glycerol, and mixtures thereof;

(c) about 0.1 to 10 wt-% of a polysiloxane copolymer of the formula



wherein R is  $-(CH_2)_3-O-(EO)_x-(PO)_y-Z$  or



n is 0 or 1; m is at least 1, Z is hydrogen or alkyl of 1-6 carbon atoms, and the weight ratio in % of EO:PO may vary from 100:0 to 0:100.

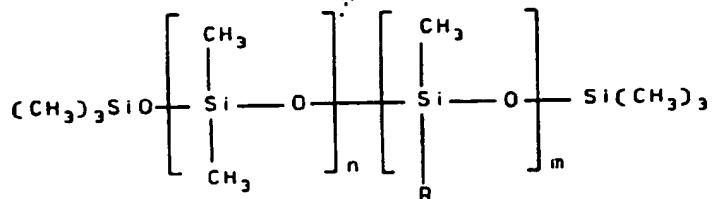
16. The composition of claim 15, wherein R is  $-(CH_2)_3-O-(EO)_x-(PO)_y-Z$ , in which Z is hydrogen, methyl or butyl and the weight ratio in % EO to PO is 100:0 to 40:60.

17. The composition of claim 16, which further comprises about 0.1 to 10 wt-% of an ethoxylated fluoroaliphatic sulfonamide alcohol.

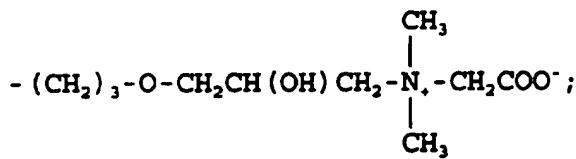
18. A method of cleaning plasticware which comprises:

(a) contacting the ware with an alkaline aqueous cleaning agent in a warewashing machine at 100-180°F to produce cleaned plasticware; and

(b) contacting the cleaned plasticware with an aqueous rinse comprising a major proportion of an aqueous diluent containing about 2 to 100 parts per million of hydrocarbon surfactants and about 0.01 to 10 parts per million of a polysiloxane copolymer of the formula



wherein R is  $-(CH_2)_3-O-(EO)_x-(PO)_y-Z$  or



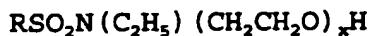
n is 0 or 1; m is at least 1, Z is hydrogen or alkyl of 1-6 carbon atoms, and the weight ratio in % of EO:PO may vary from 100:0 to 0:100.

19. The method of claim 18, wherein R is  $-(\text{CH}_2)_3 - \text{O} - (\text{EO})_x - (\text{PO})_y - \text{Z}$ , in which Z is hydrogen, methyl or butyl and the weight ratio in % EO to PO is 100:0 to 40:60.

20. The method of claim 19, wherein the aqueous rinse further comprises about 0.01 to 10 parts per million of an ethoxylated fluoroaliphatic sulfonamide alcohol.

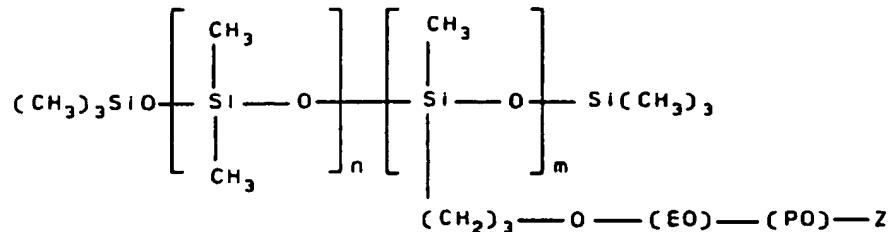
21. A rinse aid composition for plasticware, suitable for dilution to form an aqueous rinse, comprising from about 0.1 to about 10 wt-% of a fluorinated hydrocarbon nonionic surfactant and about 0.1 to about 10 wt-% of a polyalkylene oxide-modified polydimethylsiloxane in admixture with hydrocarbon surfactants.

22. The composition of claim 21, wherein the ethoxylated fluoroaliphatic sulfonamide alcohol is of the formula



wherein R is  $\text{C}_n\text{F}_{2n+1}$  in which n is 6 to 10 and x may vary from 10 to 20.

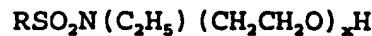
23. The composition of claim 21, wherein the polyalkylene oxide-modified polydimethylsiloxane is of the formula



wherein n is 0 or 1; m is at least 1, Z is hydrogen or alkyl from 1-6 carbon atoms and the weight ratio in % of EO:PO may vary from 100:0 to 0 to 100.

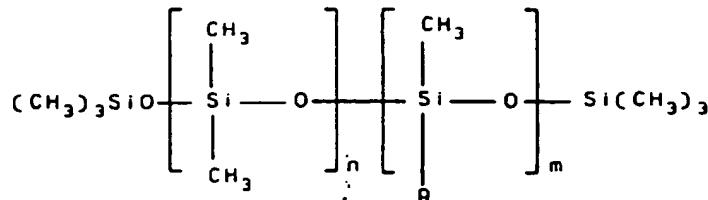
24. A rinse aid composition for plasticware, suitable for dilution to form an aqueous rinse, comprising:

- (a) about 2 to 90 wt% of one or more nonionic surfactant;
- (b) about 1 to 20 wt% of a hydrotrope;
- (c) about 0.1 to 10 wt% of an ethoxylated fluoroaliphatic sulfonamide alcohol of the formula

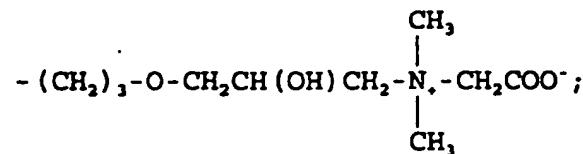


wherein R is  $\text{C}_n\text{F}_{2n+1}$  in which n is 6 to 10 and x may vary from 10 to 20; and

- (d) about 0.1 to 10 wt% of a polysiloxane copolymer of the formula



wherein R is  $-(\text{CH}_2)_3-\text{O}-(\text{EO})_x-(\text{PO})_y-\text{Z}$  or



in which n is 0 or 1; m is at least 1, Z is hydrogen, methyl or butyl, and the weight ratio in % of EO:PO may vary from 100:0 to 40:60.

# INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/US 95/05813

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C11D3/37 C11D3/16

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 511 489 (REQUEJO LUZ P ET AL) 16 April 1985 see claims 1-19; example 1; table 1 ---	1,4-8
A	US,A,4 167 488 (MURTAUGH JUSTIN J) 11 September 1979 see column 3, line 45 - column 4, line 12 ---	1,6-8
A	GB,A,2 200 365 (GOODJET LTD) 3 August 1988 see page 11, line 9 - line 14 see page 44, line 17 - page 45, line 12; claims 1,2; example 6 ---	1-4,6-8
A	EP,A,0 075 986 (PROCTER & GAMBLE ) 6 April 1983 see claims 1,2; example ---	1,4,5,9
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

23 January 1996

Date of mailing of the international search report

30. 01. 96

Name and mailing address of the ISA

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Authorized officer

Grittern, A

## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/US 95/05813

## C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 008 209 (CBS RECORDS) 20 February 1980 see claims; examples ---	1,4,6-8
A	US,A,4 302 348 (REQUEJO LUZ P) 24 November 1981 see claims -----	1,6-8

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US 95/05813

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4511489	16-04-85	AU-B-	567165	12-11-87
		AU-B-	2875084	06-12-84
		CA-A-	1225901	25-08-87
US-A-4167488	11-09-79	CA-A-	1087476	14-10-80
GB-A-2200365	03-08-88	NONE		
EP-A-0075986	06-04-83	CA-A-	1189757	02-07-85
		US-A-	4416794	22-11-83
EP-A-0008209	20-02-80	AT-T-	1428	15-08-82
		JP-C-	1381953	09-06-87
		JP-A-	55054378	21-04-80
		JP-B-	61052875	14-11-86
		US-A-	4269739	26-05-81
US-A-4302348	24-11-81	AU-B-	540606	29-11-84
		AU-B-	7425081	01-04-82
		CA-A-	1158521	13-12-83
		GB-A, B	2084175	07-04-82
		JP-A-	57085897	28-05-82

Information for preparing response for 57748US002 office action 3/30/04

Regarding the rejections:

112 2<sup>nd</sup> paragraph:

Concerning the examiner's contention that there are no definitions of low Tg and high Tg I suggest pointing the examiner to page 2 lines 12-15 which state that the A blocks have high Tg and the B block or blocks have low Tg. On page 6 line 10-14 clearly points out Tg ranges for the A block (high Tg) and page 7 line 32-page 8 line 2 clearly points out Tg ranges for the B block (low Tg). If you do not feel that just pointing this out is sufficient, the broadest numeric range i.e. greater than 20°C for high Tg and less than 20°C for low Tg could be incorporated into the claim without introducing a new limitation. As to the confusion over meltflow temperature, the meltflow temperature is clearly defined on page 3 lines 21-24.

I am not sure I understand the objection that starts "also, there are no steps..." but I would agree that claim 1 is a bit awkward as a method claim. I don't agree that selecting is not a process step. Might it be useful to rearrange the claim to combine the selecting clause and the providing clause into one step and then add a next step which is polymerizing (or forming the polymer) so that it is clearly a multistep method (selecting monomers and forming the polymer from those monomers)?

Regarding the objection to "type", I would point out to the examiner that type in this context means chemical identity as stated on page 15 lines 1-2. I would also point out that either type or chemical identity is limited to the described choices of monomers listed in the specification so I do not see how it can be viewed as extending the scope. I would not object to changing type to chemical identity if that would be a better term. Also I believe that Tg could be substituted for "type" but this would be a further restriction on the claim and I would not recommend doing this unless there is no alternative (since type brings in other factors besides Tg).

Regarding the hard and soft terminology, we have had this argument many times with examiners regarding block copolymers. Hard and soft are commonly used terms in the block copolymer art, but the terms "elastomeric" can be substituted for soft and "thermoplastic" for hard if this is clearer.

I think the examiner is saying that she is unclear the difference between the hard and soft blocks if they both have a Tg of 20°C since the Tg ranges of the hard block are 20 and above and the soft block is 20 and below. Such a polymer is unusual and not likely to be useful but if the monomers were chosen in such a way that such a polymer was formed (for example a mixture of monomer1 and monomer 2 gives an A block with a Tg of 20 and monomer 3 give as B block with a Tg of 20) and it fulfills the other requirements I don't see why that is confusing for the examiner i.e. "It can be the same block copolymer", unless she thinks that having the same Tg for the A and B blocks can only be a homopolymer. But the polymer is a block copolymer and cannot be a homopolymer.

As to the examiner's contention that there is no difference between the first monomer units and the second monomer units, while the first and second monomers can come from the same classes of monomers (i.e (meth)acrylates for example, but they cannot by definition be the same monomers or you don't have a copolymer. You cannot

for example say that the A block is a copolymer block prepared by polymerizing methyl methacrylate with methyl methacrylate.

Regarding the 102(e) rejections of 1-11 and 19-28 over Frechet US 6,663,855

The examiner concedes in the next rejection (a 103 rejection of the same claims) that Frechet does not contain the requirement of controlling the melt flow temperature of the copolymer. This limitation is the heart of the invention.

Claims 1-11 are method claims, the method being to control the melt flow temperature of a block copolymer by choosing 2 monomers to be used in the A or "hard" block. While Frechet permits the A block in his polymer to be a copolymer there is no teaching in Frechet of selecting monomers to control melt flow. Frechet's polymers are not taught to be melt flowable so how can there be a teaching method of control of melt flow.

Claims 19-28 are to block copolymers that prepared by the method of selecting monomers that control the melt flow temperature. The examiner is stating that since Frechet teaches that the A block can be a block copolymer he inherently teaches the polymers of the invention. How can Frechet teach polymers with the melt flow properties described in the invention and embodied in these claims if his polymers are not taught to be melt processable (they are placed in a carrier fluid).

Regarding the 103(a) rejections of 1-11 and 19-28 over Frechet US 6,663,855

See above. The examiner is conceding that the key restriction of all of the claims (namely the selection of a combination of 2 monomers for the A block to control the melt flow temperature of the polymer) is not taught by Frechet. There is no other reference to fill this gap in teaching, the examiner merely states that one of skill in the art would know to control the melt flow temperature by selecting 2 monomers, but I would argue that it is an unreasonable jump in logic. The examiner's reliance upon the Tg of the A block as representative of the melt flow temperature is not correct as shown in Table 15 of the present invention. This assumption is not even correct if the A block is a homopolymer. If it were correct than for example, C4 (which has an A block of homo-MMA) and C6 (which also has an A block of homo-MMA) would have the same Tg as reported by Frechet and yet their melt flow temperatures (as reflected in cross-over temperature) are very different. There is no way to take the teachings of Frechet and get to block copolymers in which the A block is comprised of at least 2 different monomers in which the monomers are selected to give control of the melt flow temperature.

Regarding the 103(a) rejections of 1-28 over Xie US 6,503,620

Xie is completely unrelated to this invention as shown in column 9 lines 13-26. The rubber-based elastomers of Xie are Kraton-like materials (e.g. styrene-isoprene-styrene) and not anything like the polymers of the invention. Xie's block copolymers have hard blocks of vinyl-aromatic monomers (e.g. styrene) and soft blocks of aliphatic conjugated dienes (e.g. isoprene).

## Dennis Daley

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**From:** lpfulton@mmm.com  
**Sent:** Wednesday, April 21, 2004 3:53 PM  
**To:** ddaley@merchant-gould.com  
**Subject:** office action 57748US002



57748US002 office  
action 3-30...

Dear Dennis,

Please see Jeff's comments below. I have not reviewed them, so I do not know if I agree with his arguments.

Regards,  
Lisa

---

Lisa Payne Fulton  
Intellectual Property Counsel  
3M Innovative Properties Company  
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Fax: 651-736-3833

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----- Forwarded by Lisa Fulton/US-Corporate/3M/US on 04/21/2004 03:50 PM

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Jeffrey M. Olofson  
3M-Corporate  
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04/21/2004 02:53  
PM  
To: Lisa Fulton/US-Corporate/3M/US@  
cc: Albert Everaerts/US-  
Jianhui Xia/US-Corporate/3M/US@3M-  
Corporate  
Subject: office action 57748US002

Lisa,  
Attached is a document with information to help you prepare a response to the office action 57748US002 "Block Copolymer Melt-processable Compositions, Methods of Their Preparation and Articles Therefrom". The office action was originally sent to outside counsel Dennis Daley but I see you listed as the current attorney so I am sending it to you. Let me know if you have any questions or need further information.

Albert and Jianhui,  
Please review and if you have other or different suggestions please send them to Lisa and copy me.  
(See attached file: 57748US002 office action 3-30-04.doc)

Regards,

Jeff

"So do all who live to see such times, but that is not for them to decide.  
All we have to decide is what to do with the time that is given to us."  
JRR Tolkien

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